WOOD AND OTHER RENEWABLE RESOURCES

Life cycle assessment of kraft lignin for polymer applications

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Abstract

Purpose Lignin is a by-product of wood pulping that is
normally used as fuel on-site (black liquor), but also has
some applications in the field of new biomaterials. This
study focuses on the life cycle inventory of lignin originat-
ing from the kraft pulping process, for polymer applications.
The system boundary includes lignin precipitation from
black liquor, washing, and drying, but excludes subsequent
application-specific *compatibilization* modifications. Lignin
transportation is considered to rely exclusively on trucking.
Methods This work is based on the *ecoinvent v2.2* database
and the IMPACT 2002+ impact assessment method. Special
attention is given to the net effect of lignin precipitation on
the mass and energy balances of the kraft process. Because
the kraft black liquor supply will far exceed the demand for
non-fuel uses for the foreseeable future, it is considered
appropriate to use either the marginal variation method of
physical allocation or a system boundary expansion. Con-
sequently, the system boundary includes natural gas as a
substitute fuel (when applicable) but excludes wood har-
vesting and the pulping process.
Results and discussion The main impacts of kraft lignin
come from the natural gas subsystem (fuel substitution and
drying) despite a significantly cleaner combustion than for
black liquor. Other significant contributors include the pro-
duction of carbon dioxide for precipitation, sulfuric acid for
washing, and sodium hydroxide to make up for sodium
losses, all of which have some improvement potential.

Conclusions The environmental profile of kraft lignin tends
to be preferable to synthetic organic compounds of similar
molecular complexity because its initial transformation
chain is relatively energy efficient. It is thus an environmen-
tally sound choice for polymer applications as long as near-
unity substitution ratios can be achieved without requiring
compatibilization modifications that are too environmental-
ly intensive and without affecting other stages of the product
life cycle. In particular, the end-of-life performance depends
on long-term lignin sequestration.

Keywords Lignin · Kraft pulping · Life cycle inventory ·
Physical allocation

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1 Introduction

After cellulose, lignin is the most abundant renewable organic
polymer, constituting between 15 and 40 % of wood by dry
weight (Doherty et al. 2011). It is a by-product of wood pulping
that is normally used as fuel on-site, as a major constituent of
the black liquor burnt in recovery boilers, but it can also be
separated and marketed. Most lignin applications are currently
based on lignosulfonates and include concrete additives, ani-
mal feed binders and additives, dust control on roads, agricul-
tural dispersants, and drilling muds. Potential applications also
include green fuels (through gasification, pyrolysis, or hydro-
liquefaction), carbon fibers, polymer fillers, resins, adhesives,
binders, and aromatic chemicals (Holladay et al. 2007).

In this study, polymer applications include fillers, where
lignin is physically blended with synthetic polymers, and
direct substitutions, where lignin participates in the poly-
merization reaction. Because all polymer applications have
the potential to take advantage of the complexity of the
lignin molecule by bypassing the transformation steps oth-
erwise required to make complex molecules out of simpler

ones, they constitute a major area of promising research on biomaterials. For example, lignin can be added as an ingredient to phenol-formaldehyde resins, displacing phenol use (and some formaldehyde), or to polyisocyanurate foams (rigid and flexible), displacing polyol use (and some isocyanate). (Bernier et al. 2011; Lautier et al. 2010). It can also be envisioned as economical filler for polypropylene, polyethylene terephthalate, polylactide, polyester resins, and other plastics, when high purity is not required.

Lignin can originate from different types of pulping processes (*sulfate* or *kraft*, *sulfite*, *soda*) and from different feedstock (hardwood, softwood, straw), resulting in potentially significant differences of environmental impacts. Consequently, LCA results cannot easily be transposed from one type of lignin to another, and the life cycle environmental impacts of many types of lignin are undocumented.

For example, Caduff et al. (2010) completed a LCA study of lignin as a raw material for binders. The study compared the impacts of lignin from two production pathways, soda pulping and bio-ethanol, to the impacts of nine chemicals and resins entering the traditional production of binders. For both pathways, the raw material was a mixture of Sarkanda grass (*Saccharum spontaneum*), wheat straw, barley straw, and rye straw. The impacts of lignin included 25 % of the impacts of the pulping process and of the straw production, on the basis of dry mass allocation. The cradle-to-gate results were generally favorable to lignin but more neutral in the case of acidification and eutrophication. Similarly, Modahl et al. (2009) completed a cradle-to-gate LCA study for the co-products of a sulfite plant in Norway, including lignin. It also used allocation on the basis of dry mass. The results did not include any product comparison based on an application-specific function. They showed that the energy used to purify each co-product explained a majority of the differential impacts between co-products. The results of these two studies are not applicable for kraft lignins because they are process-specific and feedstock-specific.

Furthermore, the choice of a mass allocation rule for pulp and lignin is questionable because the ISO standards give precedence to allocation based on relationships that "reflect the way in which the inputs and outputs are changed by quantitative changes in the products" (ISO 2006). Since such a relationship can be found by varying the quantity of lignin precipitated and then observing direct variations in the environmental loads, allocation based on that relationship becomes preferable, according to the standards, to allocation based on mass, energy, or pricing. Also, the ISO standards give even more precedence to avoiding allocation using a system boundary expansion, which is also possible in this case by measuring the combined impacts of pulp and lignin and subtracting the impacts of another kraft mill producing the same pulp without lignin. In fact, both preferred methods are equivalent when based on a single kraft plant model with a lignin production

subunit that can be switched off, as proposed in this study. Finally, note that according to the International Lignin Institute, the kraft black liquor supply exceeds the demand for non-fuel uses by the equivalent of 40–50 million tons of lignin per year. Therefore, for the foreseeable future, the pulping throughput will be determined by the paper demand and not by the demand for untransformed lignin, which will keep a lower economic value per unit mass. It is only logical that impacts independent from the lignin output, including forestry activities, remain allocated to pulp.

This article stems from two LCA studies (Bernier et al. 2011; Lautier et al. 2010) based on kraft lignin at the National Research Council Canada. Part of this program included the development of experimental additives and transformation steps to compatibilize lignin for different applications. However, these additives and transformation steps are left out of this article for the sake of generality and because industrial scale-up could still significantly affect their environmental impacts. Instead, this article focuses on the production of untransformed kraft lignin dry powder, including the major steps of precipitation, washing, and drying, for unidentified polymer applications. Special attention is given to the net effect of lignin precipitation on the mass and energy balances of the kraft pulping process, in relationship with allocation rules.

2 Methods

The work described below is based on two comparative attributional LCA studies in the context of an experimental partial substitution of petrochemicals with lignin. They were led in accordance with ISO 14040 and 14044 as confirmed by peer review. The first study (Lautier et al. 2010) covered phenol-formaldehyde resins for plywood and oriented strand board. The second study (Bernier et al. 2011) covered rigid polyisocyanurate foam for insulating panels. While these LCA reports aimed at research guidance and were targeted to a restricted audience of scientists and industrial partners, this article uses a different style aimed at providing information of general interest to a larger audience of potential lignin users. In particular, this article makes no assumptions about the performance of lignin in any application and does not define application-specific functional units because polymer formulations are still evolving, which creates uncertainties about additive requirements, transformation steps, and substitution ratios. Also, the ecotoxicological characterization of lignin was an important aspect of the original research but is not included here.

2.1 Goal and scope definition

Because this LCA evaluates lignin independently from any application, the functional unit is simply 1 kg of untransformed

dry kraft lignin powder. Comparisons between lignin and other compounds are considered outside the scope of this article. They rather belong to future cradle-to-grave studies ideally based on application-specific functional units, on better-known product compositions, and on a proper consideration of indirect effects on product life cycle. For example, if the presence of lignin in insulating foam unexpectedly affects the amount of blowing agent lost during fabrication or through permeation, the life cycle environmental performance could differ significantly and should be accounted for in an application-specific LCA.

This study is based on the *ecoinvent v2.2* database and its default European context (as opposed to the original phenol-formaldehyde and polyisocyanurate studies, which used *ecoinvent* v2.0 with modifications to better represent the Canadian context).

This LCA can be considered *cradle-to-gate*. However, in many polymer applications, lignin can be expected to perform similarly to the substituted compounds, which should not affect infrastructure, packaging, distribution, installation, use, or end-of-life. In such cases, it should be relatively simple to transpose this study into *cradle-to-grave* comparative results. However, this would still require new LCAs based on the functional unit of each specific application and on an appropriate experimental measurement of long-term lignin sequestration. It should be noted that lignin is relatively difficult to degrade, even in the context of natural wood decay, and likely even more so when embedded within inert products.

2.2 Inventory method and data

Figure 1 shows the major steps of lignin recovery in a kraft pulp mill and the corresponding life cycle inventory system boundary. The inventory was established with the help of *FPInnovations*, a Canadian private, nonprofit forest research institute that has developed such a lignin recovery process (Kouisni 2011). Some technical details related to the phenol-formaldehyde resin study have been published by Kouisni et al. (2011).

Allocation is performed by comparing emissions with and without lignin recovery for the same mill and assigning the differences to lignin. This corresponds to the marginal variation method of establishing allocation on the basis of a physical relation (Jolliet et al. 2005). However, it can also be seen as a system boundary expansion in which the avoided product is pulp from a separate kraft mill not recovering lignin. In effect, this puts large parts of the pulping process (wood harvesting, bleaching, calcium cycle, etc.) outside the system boundary in Fig. 1. Such a disconnection between the life cycle inventories of lignin and pulp is coherent with the fact that the pulping throughput will be determined exclusively by the paper demand for the foreseeable future, as indicated in Section 1. Table 1 summarizes the *ecoinvent* processes used to model the life cycle inventory of kraft lignin.

2.2.1 Mass balance and CO_2 emissions

At the precipitation step, industrial-grade CO_2 is injected in the black liquor in order to decrease its pH. (The related *ecoinvent* process in Table 1 is based on CO_2 recovery and liquefaction in ammonia plants.) Lignin then partially precipitates, in decreasing order of molecular weight. A small amount of H_2S is also emitted and neutralized in the existing non-condensing gas scrubber, consuming NaOH in an additional quantity assumed to be stoichiometric. The remaining black liquor is recycled to the multi-effect evaporators and recovery boiler (see Fig. 1), where it is burned as it would normally be, despite its heating value being partially depleted. The injected CO_2 is assumed to be re-emitted there, because the amount of CO_2 captured in the smelt sent to recausticizing (as Na_2CO_3) is constrained by the available sodium.

The precipitated lignin is wet and needs to be filtered, washed, and dried in the subsequent steps in Fig. 1. The filtrate from the filtration step, which consists of lignin-depleted black liquor, is recycled to the multi-effect evaporators. Washing is performed with water and H_2SO_4, some of which is neutralized by the remaining traces of black liquor. The washing effluent, which is more dilute than the filtrate and contains excess H_2SO_4, is neutralized at the wastewater treatment plant by increasing the lime mud bleeding rate, indirectly increasing make-up $CaCO_3$ purchases. In Fig. 1, this is shown as a $CaCO_3$ input between recausticizing and the lime kiln, which are two processes remaining outside the system boundary because their operation (and CO_2 emissions) is independent of lignin production. As a worst case scenario, additional $CaCO_3$ is assumed to be required in the same amount as H_2SO_4. Optionally, the washing effluent can be sent to the multi-effect evaporators, increasing steam requirements (not shown in Fig. 1).

The mass balance should be coherent with the marginal variation method of physical allocation for each atomic element including Na, S, and C. In particular, additional NaOH must be required somewhere in order to replace the sodium entrained at the washing step. Note that recycling the washing effluent back to the multi-effect evaporators in order to recover its sodium can be counterproductive if additional NaOH is required to re-establish a proper Na/S balance. For the carbon balance, 1 kg of lignin is considered to sequester up to 2.3 kg of CO_2, corresponding to a lignin composition of 62 % C, the average of four samples provided by FPInnovations. Consequently, the net mass balance for the recovery of kraft lignin involves increased inputs for CO_2, H_2SO_4, NaOH, $CaCO_3$, and water, as indicated in Table 1, as well as decreased net CO_2 emissions and increased emissions of relatively harmless sodium, calcium, and sulfate ions to water. Emissions of atmospheric pollutants and waterborne organic contaminants, which are not significant in the overall mass balance, are described separately in Sections 2.2.3 and 2.2.4, respectively.
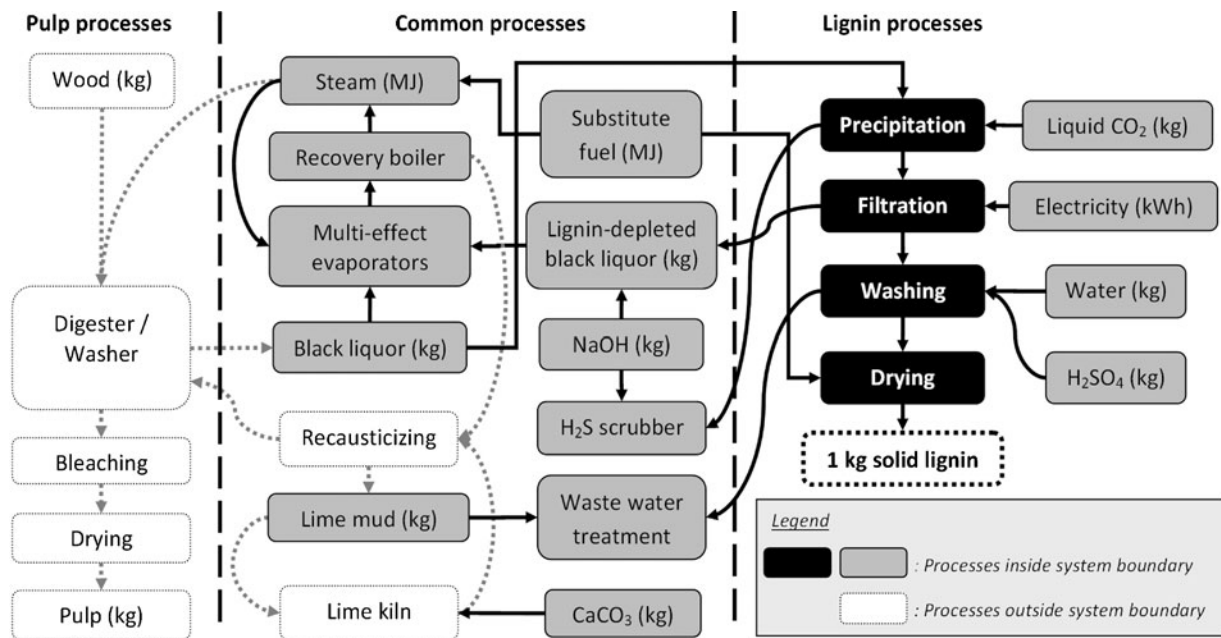
Fig. 1 System boundary for the kraft lignin life cycle inventory

2.2.2 Energy balance

According to the marginal variation method of physical allocation, differences in the kraft mill energy balance, such as additional steam consumption *per unit pulp*, are attributable to lignin. The quantity of steam required to substitute the lost output from the recovery boiler system is assumed to be 26.8 MJ/kg lignin, which is the average higher heating value of the same four samples provided by FPInnovations. However, this value can decrease if a larger fraction of the water initially present in the black liquor can be condensed in the multi-effect evaporators, which is a reasonable hypothesis since there are less solids to carry, but can be limited by mechanical complications. Another 4.7 MJ/kg lignin of steam energy is used for drying. In order to accurately reflect the net effects of such increases in steam demand, a few cases are possible:

1. If lignin precipitation is used to de-bottleneck the recovery boiler, a likely outcome is that the biomass energy available on-site will remain proportional to the pulp output and only fossil fuels will be consumed to generate additional steam to complete the energy balance of the kraft mill.

2. If excess hog fuel and the corresponding spare boiler capacity are both available, they can be used to produce the required steam, with some fossil fuel support depending on humidity. However, this renewable resource can be regionally constrained, i.e., its consumption may sometimes reduce the supply for other hog fuel consumers within a reasonable trucking distance.

3. If lignin precipitation is used to de-bottleneck the recovery boiler and there is no spare hog fuel boiler capacity, it is also possible that *less* hog fuel can be used per unit pulp, causing an incremental fossil fuel demand in excess of the incremental steam demand per unit pulp.

4. It is also possible that the additional steam requirement affects the electricity balance, depending on the spare capacity in the steam turbines, on the relative prices of

Table 1 Inventory of 1 kg untransformed dry kraft lignin powder (using natural gas) based on *ecoinvent* v2.2

Input	Unit	Quantity	*ecoinvent* process name
Natural gas	MJ	31.5	Natural gas, burned in industrial furnace >100 kW/RER
CO_2	kg	0.30	Carbon dioxide liquid, at plant/RER
H_2SO_4	kg	0.230	Sulfuric acid, liquid, at plant/RER
NaOH	kg	0.107	Sodium hydroxide, 50 % in H_2O, production mix, at plant/RER
$CaCO_3$	kg	0.230	Limestone, milled, packed, at plant/CH
Water	kg	4.85	Tap water, at user/RER
Electricity	kWh	0.010	Electricity, medium voltage, production UCTE, at grid/UCTE
Trucking	tkm	0.934	Transport, lorry 16–32 t, EURO4/RER

fossil fuels and electricity, and on the pinch conditions in the steam network. For example, additional steam production through a back-pressure turbine can result in additional electricity production, in which case the fuel consumption would increase *faster* than the steam consumption. Comparatively, in a high-efficiency greenfield kraft mill, lignin recovery is likely an opportunity to remove a condensing turbine from the design, leaving fuel consumption unchanged but reducing the electricity production (Wising et al. 2006).

The present study considers that the first case above is more reflective of industry practice as recovery boiler de-bottlenecking in old kraft mills with access to low-cost natural gas is expected to be an important initial motivation for lignin recovery. Lacking any better data, cases 2, 3, and 4 above are assumed to cancel each other out when averaging scenarios from different kraft mills. Consequently, natural gas as a substitute fuel becomes a major component of the lignin life cycle, and the electricity input in Table 1 corresponds to the filtration step only. The results of this study may be somewhat inaccurate for lignin produced in a context different than the de-bottlenecking of recovery boilers in old kraft mills with access to low-cost natural gas.

It is important to consider transportation, which represents an unusually large fraction of the cumulative energy demand in this case, because kraft mills are often remote from consumption centers and tend to rely on trucking. Consequently, lignin transportation distances can become a sensitive parameter (Bernier et al. 2011). This study considers that chemical inputs and lignin itself are transported for 500 km, implying that lignin is transported 500 km *more by truck* than other compounds it could potentially replace.

2.2.3 Boiler emissions

The combustion of a substitute fuel such as natural gas generates emissions attributable to lignin, which are offset by the recovery boiler emissions reduction caused by a lower black liquor heating value. These negative emissions have to be estimated using a model because they have not yet been measured in a full-scale recovery boiler burning lignin-depleted black liquor. Comparatively, atmospheric emissions other than from boiler systems are considered outside the system boundary because they remain approximately proportional to the pulp output in all cases.

In the recovery boiler, changes in emissions are difficult to predict because a different flame temperature profile is likely to yield a different flue gas composition. For instance, a lower concentration of sodium vapors could precipitate less Na_2SO_4 and result in higher sulfur emissions (SO_2, H_2S, and others). According to Wising et al. (2006), higher SO_2 emissions are expected, but according to FPInnovations, it is possible to keep emissions constant per unit of heat flow by properly balancing the various air inputs to the recovery boiler (personal communication). Lacking experimental data, this study assumes that the recovery boiler emissions of NO_x, SO_x, H_2S, and particulates (mostly Na_2SO_4 and Na_2CO_3 rather than soot) correspond to the average of the estimates of the European Commission (IPPC 2001) and are proportional to the black liquor heating value (12.8 MJ/kg before lignin extraction) independently of pH or composition. Implicitly, recovery boiler emissions of other substances are insignificant or remain constant per unit pulp.

When de-bottlenecking the recovery boiler, its power output remains constant while its smelt output—and ultimately the pulp production—increases. Because recovery boiler emissions are then assumed to remain also constant per unit time, they decrease per unit pulp in the recovery boiler but not elsewhere. In effect, the combustion credit is 2.1 kg black liquor/kg lignin (1 MJ for 1 MJ) no matter if the pulp output increases or not. (A more conservative assumption would be 1 kg for 1 kg.) On-site atmospheric emissions attributable to lignin recovery are always negative overall because natural gas is a cleaner burning fuel than black liquor. (That may not be the case if hog fuel is used instead.)

2.2.4 Emissions to water

The lignin washing wastewater (see Fig. 1) is chemically similar to diluted black liquor, except that it is acidic and contains less high-molecular-weight lignin compounds that tend to resist biodegradation. However, the remaining fraction is not necessarily entirely biodegradable during treatment, and its impact on aquatic eutrophication and ecotoxicity can be expected to be similar to any effluent spiked with black liquor. Also, lignin in water is known to have a long half-life and to be slightly toxic, which may be related to the release of low-molecular-weight phenolic compounds (Pessala et al. 2010). Thus, emissions to water can be associated both to the washing effluent and to potential end-of-life scenarios where some lignin leaching from end products enters the aquatic environment.

The co-treatment of other kraft mill effluents with the lignin washing wastewater can reduce the overall treatment effectiveness via a reduced residence time and/or toxic effects on some of the microorganisms in the system. According to the marginal variation method of physical allocation, any such indirect impact on aquatic eutrophication and ecotoxicity is entirely attributable to lignin.

The net effects of the lignin washing wastewater after treatment are not necessarily significant relative to the impacts of the overall pulp production or even measurable through monitoring, but can still represent a large ecological footprint relative to the synthetic products comparable with lignin for polymer applications. For this reason, these effects

are considered a significant source of unknown impacts in this study.

2.3 Impact assessment method and software

Potential environmental impacts are evaluated using the IMPACT 2002+ v2.10 method (Jolliet et al. 2003) using the SimaPro 7.3.2 software, for the functional unit of 1 kg dry product.

2.4 Critical review

The two LCA reports for the phenol-formaldehyde and polyisocyanurate studies (Bernier et al. 2011; Lautier et al. 2010), from which this article is based, were both reviewed by Dr Sébastien Humbert, scientific director at Quantis Intl.

3 Results

Figure 2 shows a contribution analysis for the mid-point categories. It shows that avoided emissions, steam production using natural gas, chemicals, and transportation, are all significant contributors in many impact categories each. The production of liquid CO_2, H_2SO_4, and $NaOH$ together represent more than 50 % of the overall impacts in four categories, mostly due to electricity consumption (CO_2 and $NaOH$) and process SO_2 emissions (H_2SO_4).

In the case of climate change, the "process emissions" in Fig. 2 correspond to the difference between the CO_2 permanently sequestered in lignin (best case) and the re-emission of the CO_2 used for precipitation. The on-site CO_2 emissions from natural gas combustion are part of the "natural gas" subsystem. With 100 % sequestration, these emissions nearly cancel each other, and the net life cycle impact is only 0.6 kg CO_{2eq}/kg lignin. One-hundred percent sequestration implies that lignin will be embedded in a polymer that prevents its degradation for the relevant time frame. This allows a fair comparison with other polymer cradle-to-gate data. If the polymer is incinerated, an LCA for that polymer would have to consider CO_2 emissions from both lignin and fossil carbon.

In the case of respiratory inorganics (and human health in general), the avoided particulate emissions from the recovery boiler play an important role. However, real impacts are somewhat uncertain depending on the health effects of Na_2SO_4 and Na_2CO_3 particulates specifically, on the position of the mill relative to urban centers, and on how successfully the flame temperature profile can be fine-tuned in practice.

Three categories are absent in Fig. 2 because of data constraints. In the case of aquatic eutrophication and ecotoxicity, there are important unknown impacts (see Section 2.2.4), and

the results are considered too uncertain. In the case of land occupation, the total impact becomes significant (relative to the pulp co-product) only if some forest use is allocated to lignin, which is incompatible with the ISO-compliant allocation method used in this case. It does not appear conceivable that the demand for trees could vary as a *consequence* of a varying demand for lignin, nor does it appear good practice to conclude otherwise using mass or energy allocation.

Table 2 summarizes the mid-point results.

Figure 3 illustrates the impacts of 1 kg untransformed dry kraft lignin powder (using natural gas) with and without end-product transportation, of 1 kg kraft (sulfate) pulp, and of 1 kg of different polymers and ingredients, for the four end-point categories within IMPACT 2002+ and for aquatic acidification. All items other than lignin are based on the *ecoinvent* v2.2 processes of the same name, respectively. All results are normalized to the worst item in each category, but should not be taken as directly comparable since there is no functional equivalence. Comparisons between lignin and other products only give an idea of the margin available for *compatibilization* modifications.

Figure 3 shows that the environmental performance of kraft lignin for "Human health," "Climate change," and "Resources" tends to be favorable, despite some conservative assumptions such as the black liquor substitution with a fossil fuel instead of renewable hog fuel. For "Ecosystem quality," a category in which the petrochemical industry is not a large contributor in general, the lignin performance is close to the median. Finally, the lignin performance for "Aquatic acidification" is somewhat penalized because of SO_2 emissions related to H_2SO_4 and natural gas production.

4 Discussion

Kraft lignin and kraft pulp have very different impact profiles because lignin essentially becomes a virtual product of natural gas, not wood, following the marginal variation method of physical allocation (or system boundary expansion; see Section 2.2). In particular, Fig. 3 shows that lignin, relative to pulp, generates less impacts on ecosystem quality but more on non-renewable resources and climate change. These differences would not arise if the impacts of kraft pulping were instead allocated on a mass basis between pulp and lignin, in which case the impacts of 1 kg lignin before precipitation would be exactly equal to the impacts of 1 kg pulp before bleaching (sulphate pulp in Fig. 3).

In general, comparisons between fossil fuel products and bio-products tend to generate inconclusive LCA results, no matter the application, because of some trade-off between impact categories that are difficult to
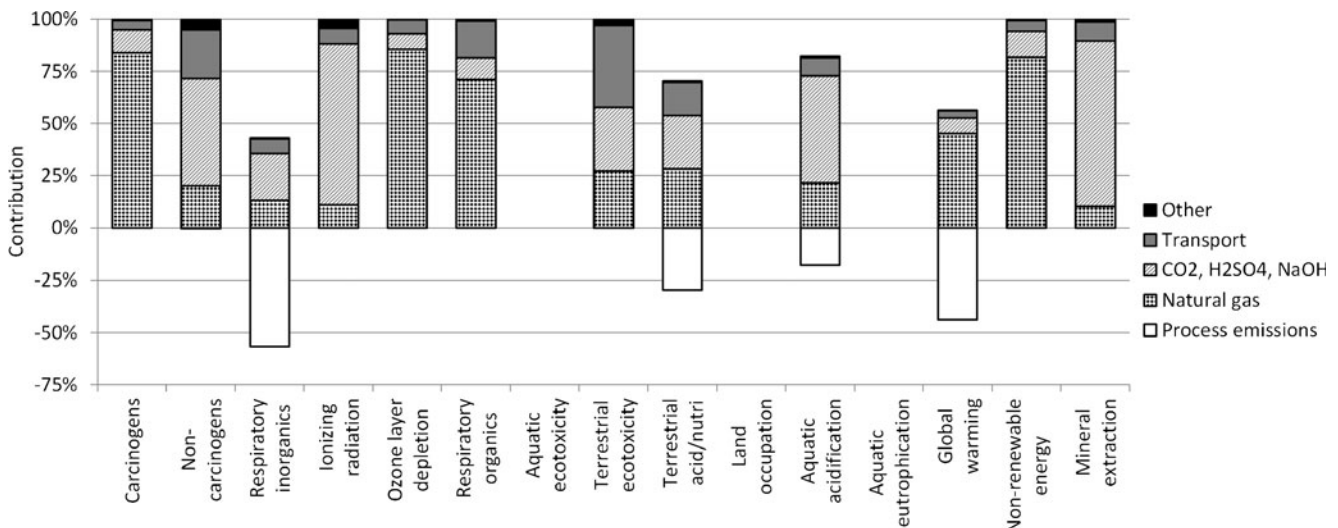
Fig. 2 Process contribution analysis for kraft lignin using IMPACT 2002+ mid-point categories

aggregate such as land occupation by forestry and petroleum extraction. However, such a trade-off is not present for all bio-products, because a variation in the output flow causes no variation in agricultural and forestry activities *in some cases*, a physical reality that should not be obscured by misguided allocation methods. Bio-products based on raw biomass previously used as fuel by default, such as lignin, provide a counterexample. For these bio-products, it is reasonable to expect LCA results in most categories to correlate to the transformation efficiency of each scenario and to expect a clear-cut conclusion if one scenario is more efficient. According to Fig. 3, untransformed lignin appears

Table 2 LCA for 1 kg untransformed dry kraft lignin powder using IMPACT 2002+ mid-point categories

Category	Unit	Quantity
Carcinogens	kg C_2H_3Cl eq	2.3E−02
Non-carcinogens	kg C_2H_3Cl eq	6.9E−03
Respiratory inorganics	kg $PM_{2.5}$ eq	−2.7E−04
Ionizing radiation	Bq C-14 eq	2.1E+01
Ozone layer depletion	kg CFC-11 eq	3.6E−07
Respiratory organics	kg C_2H_4 eq	5.3E−04
Aquatic ecotoxicity	kg TEG water	N/A
Terrestrial ecotoxicity	kg TEG soil	1.8E+01
Terrestrial acid/nutri	kg SO_2 eq	1.2E−02
Land occupation	m^2 org. arable	N/A
Aquatic acidification	kg SO_2 eq	5.3E−03
Aquatic eutrophication	kg PO_4 P-lim	N/A
Global warming	kg CO_2 eq	5.7E−01
Non-renewable energy	MJ primary	4.8E+01
Mineral extraction	MJ surplus	1.4E−02

uncompromisingly advantageous, for most impact categories and under a wide range of sensitivity analysis scenarios, in cases where it can be used directly with a near-unity substitution ratio in a polymer application. Comparatively, the use of transformed lignin can be expected to add significant impacts if it relies on large amounts of chemicals, repetitive dryings, and/or sophisticated additives (e.g., for compatibilization).

It is important to note that the environmental benefits of lignin originate differently depending on the application. In direct substitution applications where lignin is expected to be functionally equivalent to the displaced monomer, the benefit is straightforward, but compatibilization is more likely to be required in order for the polymerization reaction to work properly. Comparatively, in polymer filler applications, the benefit is more convoluted because lignin can only accomplish a *filler* function while the polymer being diluted can accomplish both the filler and the application-specific functions, which is not strictly equivalent. It would arguably be fairer to compare lignin with other potential fillers when available.

The environmental performance of kraft lignin, even untransformed, can be improved. Measures to reduce H_2SO_4 and NaOH consumption would be particularly attractive to investigate because the other inputs are either unavoidable or insignificant contributors. Also, the production of on-site CO_2 could be investigated, for example by operating the lime kiln using pure oxygen. Finally, the procurement of H_2SO_4 from specific suppliers with low emissions would significantly reduce impacts on human health and acidification. SO_2 emissions can be reduced by up to 98 % during H_2SO_4 production using various process-integrated and end-of-pipe technologies (Wiesenberger and Kirchner 2001).
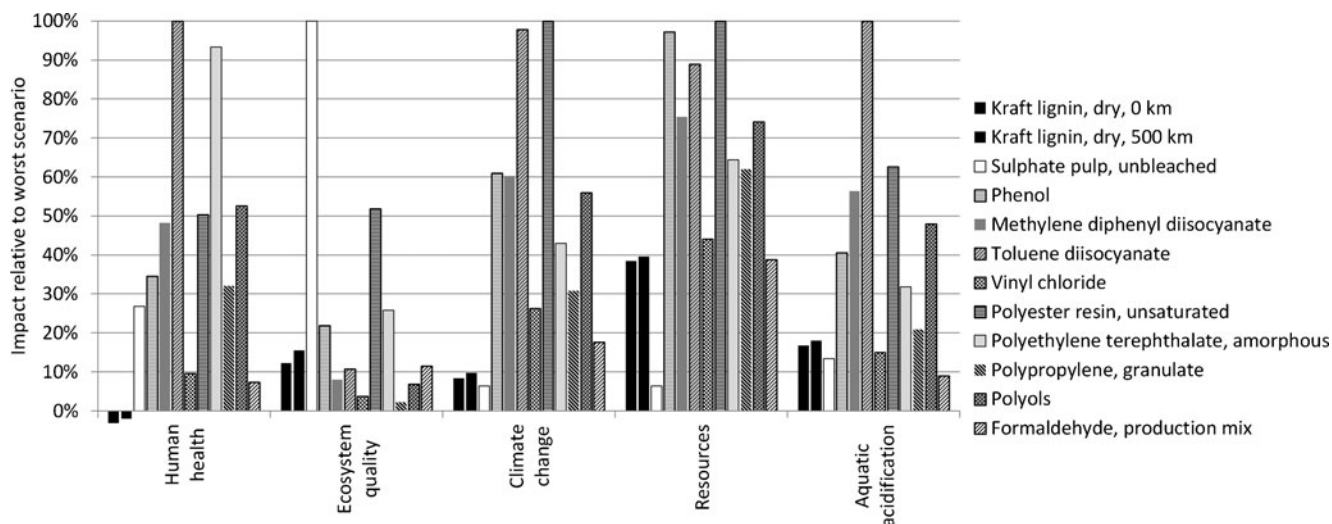
Fig. 3 Comparative assessment for kraft lignin with and without trucking, kraft pulp, and some polymers (and ingredients); these are *not* functionally equivalent

The impacts of different pathways to lignin production, including non-kraft lignins and lignosulfonates, cannot be directly compared because the other studies mentioned in the introduction have not used the same allocation method. By following the marginal variation method of physical allocation, many feedstock-specific processes are excluded from the system boundary, and the LCA results become less dependent on the type of pulping process. Consequently, the comparison between different lignins is expected to depend more on the quantity of required chemicals, on the transportation distance, and on thermal synergies (such as in the multi-effect evaporators). This stresses the importance of using chemicals efficiently in order to produce kraft lignins competitively.

Finally, despite the large potential benefits of using lignin for polymer applications, significant unknown impacts remain for the aquatic ecotoxicity and eutrophication categories. They occur when lignin and derivatives, originating from the washing step or from some end-of-life scenarios, enter the aquatic environment. Further investigation of the toxicity and environmental fate of lignin would reduce uncertainties in these categories and improve the overall assessment.

5 Conclusions

The life cycle assessment of wood pulp joint secondary co-products such as dry lignin powder requires a careful consideration of allocation methods. The marginal variation method of physical allocation is appropriate when the co-product output can effectively be varied, as is the case with lignin. Consequently, this study has shown that kraft lignin and kraft pulp have different environmental profiles. In particular, the impacts of lignin on land occupation and ecosystem quality are insignificant relative to pulp and many other biomaterials because lignin, being in surplus with respect to non-fuel uses, is effectively a virtual product of natural gas. As a result, untransformed kraft lignin is favorably comparable to synthetic organic compounds of similar molecular complexity in general, in large part because it can be recovered after only a few steps. To minimize the environmental impacts of kraft lignin, it is important to optimize the consumption of chemicals such as CO_2, H_2SO_4, and NaOH.

For polymer applications, the impacts of kraft lignin also depend on subsequent transformation steps, on substitution ratios, and on potential indirect effects on other life cycle stages. After these applications become more developed, these impacts can be further investigated by application-specific cradle-to-grave comparative studies. One particular concern is the potential release of lignin degradation products during the polymer end-of-life, potentially impacting aquatic ecotoxicity, aquatic eutrophication, and climate change.

Recent research at the National Research Council Canada has shown specifically that untransformed lignin can be environmentally preferable to a polyester polyol in a polyisocyanurate foam application and to phenol in a phenol-formaldehyde resin application, if the product performance can be proven to be satisfactory. This illustrates how LCA can provide useful guidance in the context of biomaterials research and development. Research is ongoing to determine whether lignin can be compatibilized for these applications with a limited amount of transformation. Research is also ongoing to determine the ecotoxicological effects of lignin and their relationship with phenolic compounds.

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